Standard Project

Experimental Report

Proposal title: Phase transition, crystal strains and microcracking coupling in bulk pure zirconia polycrystals probed by in situ high temperature X-ray diffraction	**Proposal number**: 02-02-872

Beamlines: D2AM	**Dates of experiment**: 14th to 20th Sept. 2021	**Date of report**: Nov. 2021
Shifts: 18	**Local contact**: G. Chahine	*Date of submission:*

Objective & expected results:

The aim of the experiment was to follow *in situ* the phase transition process between the tetragonal (t) and monoclinic (m) pure zirconia phases in a dense zirconia polycrystal. This proposal is part of a general study devoted to the determination of the influence of internal residual stresses into such martensitic phase transition. According to previous experiments, we aim to follow this phase transition through *in situ* 3D reciprocal space mapping using the QMAX furnace [1] implemented on the D2AM beamline.

We have shown previously that the m→t and t→m phase transition in such pure zirconia polycrystals are spread over up to one thousand degree and are strongly related to strain relaxation process [2, 3]. We expected two different types of result. First of all, the measurement of the evolution of the position of both the monoclinic and tetragonal reciprocal lattice nodes (RLNs) all along the phase transition process will allow us to determine the true thermal expansion under internal stresses along the main crystal symmetry axis during the loss of these symmetry axis through the transition between the 4/m m m tetragonal punctual group to the 2/m monoclinic punctual group. The second point is related to the possible relationship between the diffuse scattering intensity and the value of the order parameter of this phase transition.

Results and conclusions of the study:

The 3D reciprocal space maps (RSMs) recorded the 111_t RLN[1] at room temperature and at 1250 °C are reported Fig. 1. The splitting, observed at room temperature, of this tetragonal node to a number of monoclinic RLNs is a very clear illustration of the twinning process associated to the t→m solid-state phase transition (SPT). We followed this process continuously as function of the temperature during heating and cooling processes. Some of the 3D maps recorded near the 111_t RLN are reported in Fig. 2. Similar measurements close to the 202_t and 220_t RLNs were also done.

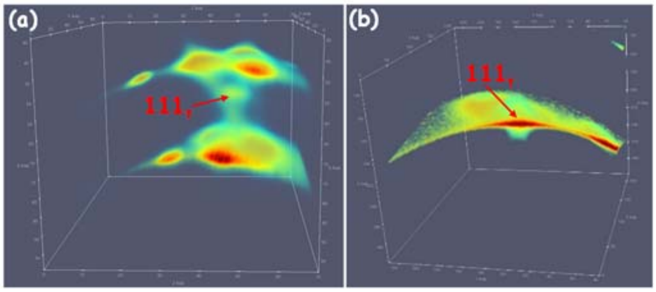

Fig. 1. 3D-RSMs around the 111_t node. (a) at room temperature ; (b) at 1250 °C.

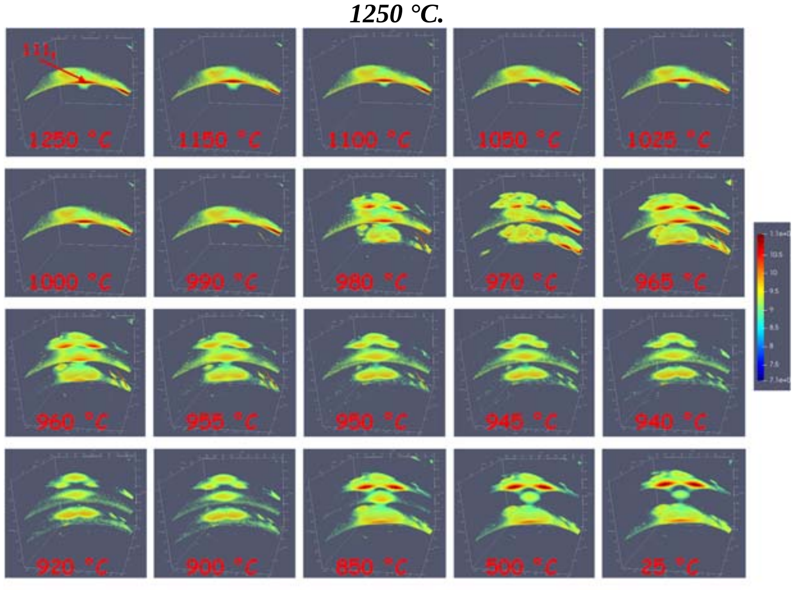

Fig. 2. Evolution of the 3D-RSMs as a function of the temperature near the 111_t node during cooling from 1250 °C to room temperature

Considering one tetragonal crystal, six different orientations of the monoclinic cell are possible. Three intensity maxima, located in symmetric position are clearly observed both on the $(\bar{1}11)_m$ and $(111)_m$ Debye-Scherrer rings. They correspond to six different monoclinic RLNs. Following the loss of this $<111>_t$ symmetry axis *in situ* as a function of the temperature corresponds to a dynamic study of this twinning process. The amplitude of the splitting of the 111_t RLN through the t→m SPT is directly related to the value of the β angle of monoclinic zirconia and the value of

[1] note that in all the cases, the tetragonal zirconia ($P4_2/nmc$) is described in the pseudo-cubic setting, *i.e.* a “tetragonal face centered” lattice corresponding to the setting ($Fm\bar{3}m$) of the cubic native crystal.

this angle evolves continuously as a function of the temperature, and it also depends on the internal stress state. Accurate evaluation of the respective angular positions of all the RLN centers will be done in order to describe quantitatively this twinning process under internal stresses. The knowledge of the evolution of the position of the RLNs as a function of the temperature is the illustration of the thermal expansion under stresses. The determination of these positions will thus allow us to extract information on the influence of residual stresses onto the t→m SPT.

According to our previous measurements [3], the β angle evolves between 99.5 at room temperature to 98.7 at 1000 °C. Such a gap between these values and 90° (for the tetragonal lattice) results in a quite large splitting in the reciprocal space allowing to clearly distinguish the 111_t RLN and all the 111_m and $\bar{1}11_m$ monoclinic RLNs (see Fig.1.). As a consequence, the diffuse scattering spreading into the split RLNs is reasonably visible and could be in principle disentangled from the Bragg peaks contributions. As discussed in [3], because zirconia crystals are made of pure zirconia, the diffuse scattering signal is certainly mainly related to strains and its intensity along a direction defined by two opposite monoclinic RLNs is a measurement of the *d*-spacing distribution along the normal to the diffracting planes. We have shown that in such polycrystal the t→m SPT can be formally described as a second order SPT [3]. According to this approach, we will develop a formal analysis of this signal that could illustrate the evolution of the order parameter through the phase transition process.

Justification and comment about use of beamtime

The D2AM beamline associated to the QMAX furnace is very well adapted to such high temperature *in situ* study. We used the 2D-detector (D5 Hybrid pixel detector) available on the beamline, the energy of x-ray beam was fixed at 17.9 keV and the sample to detector distance was equal to 0.80 m. In such configuration, reciprocal space slices with a convenient size without any angular displacement of the detector can be record and the full measurement of one 3D RSM take 60 minutes. Taking into account the SPT process that we are studying this duration is very well suited. This experiment using synchrotron radiation was the first one of the French-German HoTMiX project, it was a success and really interesting data have been collected.

References

[1] R. Guinebretière, S. Arnaud, N. Blanc, N. Boudet, E. Thune, D. Babonneau, O. Castelnau, Full reciprocal space mapping up to 2000 K under controlled atmosphere: the multi-purpose QMAX furnace, J. Appl. Cryst. 53 (2020) 650-661.

[2] T. Ors, F. Gouraud, V. Michel, M. Huger, N. Gey, J. S. Micha, O. Castelnau, R. Guinebretière, Huge local elastic strains in bulk nanostructured pure zirconia materials, Mater. Sci. Eng. A 806 (2021) 140817.

[3] R. Guinebretière, T. Ors, V. Michel, E. Thune, M. Huger, S. Arnaud, N. Blanc, N. Boudet, O. Castelnau, Coupling between elastic strains and phase transition in dense pure zirconia polycrystals, Phys. Rev. Mater. 6 (2022) 013602.